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(54) PRODUCTION OF POLYARYLENE SULFIDE

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a method for producing a polyarylene sulfide, capable of carrying out reduction of cost accompanied by recovery and purification treatments of an organic amide solvent after finishing polymerization reaction and excellent in mechanical strength, melt stability, moldability, or the like.
SOLUTION: This method for producing a polyarylene sulfide comprises (A) a process for heating a mixture containing an organic amide solvent, an alkali metal sulfide and a dihalo-aromatic compound to react the alkali metal sulfide with the dihalo-aromatic compound, and adding water to the reaction system at a desired point of time from starting of the reaction to finishing of the reaction so that water enough to form separated state of liquid-liquid phase comprising condensed phase and diluted phase of produced polymer exists during reaction, and continuing heating reaction until the reaction is finished and (B) a process for evaporating or distilling the organic amide solvent from the reaction mixture comprising the organic amide solvent, produced polymer, water and an alkali metal halide produced as a by-product to recover the organic amide solvent, in a method for producing a polyarylene sulfide by reacting an alkali metal sulfide with a dihaloaromatic compound in an organic amide solvent.

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CLAIMS

[Claim(s)]
[Claim 1] In the approach of making an alkali-metal sulfide and a dihalo aromatic compound reacting, and manufacturing the poly arylene sulfide in an organic amide solvent (A) While heating an organic amide solvent, an alkali-metal sulfide, and the mixture containing a dihalo aromatic compound and making them react Add water in the system of reaction and the water of the amount which is sufficient for making the liquid-liquid phase separation condition which consists of the dense phase and lean phase of a generation polymer by it form is made to exist at the event of the request during [from after reaction initiation] before reaction termination. Subsequently A pyrogenetic reaction is made to continue till reaction termination. And after (B) reaction termination, an organic amide solvent, The manufacture approach of the poly arylene sulfide characterized by including each process which is made to evaporate or distill an organic amide solvent, and collects them from a generation polymer, water, and the reaction mixture containing byproduction alkali-metal halide.
[Claim 2] The manufacture approach according to claim 1 which includes further each process which rinses the mixture containing the generation polymer which remains after the solvent recovery from the (C) reaction mixture, and byproduction alkali-metal halide after a solvent recovery process (B), and removes alkali-metal halide, and dries the humid polymer after (D) rinsing.
[Claim 3] The manufacture approach according to claim 2 which includes further the process which (E) desiccation polymer is heat-treated [process] after a desiccation process (D), and increases the melt viscosity of a polymer.
[Claim 4] The manufacture approach given in claim 1 which continues a pyrogenetic reaction till reaction termination in the state of this liquid-liquid phase separation while adding water and making a liquid-liquid phase separation condition form by it in the system of reaction in a reaction process (A), when the invert ratio of a dihalo aromatic compound becomes 50 - 98-mol the range which is % after reaction initiation thru/or any 1 term of 3.
[Claim 5] The manufacture approach given in claim 1 which arranges the process which precedes recovery of an organic amide solvent, is made to evaporate or distill some [at least] water, and removes it from a reaction mixture in a solvent recovery process (B) thru/or any 1 term of 4.
[Claim 6] The manufacture approach given in claim 1 which evaporates an organic amide solvent with a flash method in a solvent recovery process (B) thru/or any 1 term of 5.
[Claim 7] The manufacture approach according to claim 3 heat-treated under existence of oxygen in a heat treatment process (E) with the heat treatment temperature of 150 degrees C or more and under the melting point of a polymer.
[Claim 8] The manufacture approach according to claim 3 of increasing the temperature of 310 degrees C, and the melt viscosity of the polymer measured in the 1200/second of shear rates in a heat treatment process (E) by the R/C of 1.3 times or more of the melt viscosity of a desiccation polymer.
[Claim 9] In a reaction process (A), in the condition that 0.5-2.0 mols [per one mol of (1) preceding paragraph process:preparation alkali-metal sulfides] water exists React in a 180-235-degree C temperature requirement, and a prepolymer is made to generate at invert ratio % of 50-98 mols of a

dihalo aromatic compound. Subsequently (2) -- latter-part process:, while adding water so that it may be in the condition that an excess of 2.0 mol per one mol of preparation alkali-metal sulfides and water 10.0 mols or less exist in the system of reaction The manufacture approach given in claim 1 which makes a polymer generate by the approach of carrying out temperature up into a 245-290-degree C temperature requirement, and continuing a pyrogenetic reaction thru/or any 1 term of 8.

[Claim 10] In a reaction process (A), in the organic amide solvent containing 0.5-2.0 mols [per one mol of (1) process 1:preparation alkali-metal sulfides] water An alkali-metal sulfide and a dihalo aromatic compound are made to react in a 170-270-degree C temperature requirement. Make it react in that case, carrying out temperature up of the between from at least 220 degrees C to 240 degrees C of this temperature requirement with an average of 0.1-1-degree-C programming rate for /, and a prepolymer is made to generate at invert ratio % of 50-98 mols of a dihalo aromatic compound. Subsequently (2) While adding water at the temperature of 235 degrees C or more in the system of reaction so that it may be in the condition that an excess of process 2:2.0 mol per one mol of preparation alkali-metal sulfides and water ten mols or less exist The manufacture approach given in claim 1 which makes a polymer generate by the approach of continuing a reaction in a 245-290-degree C temperature requirement thru/or any 1 term of 8.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the approach of manufacturing economically the poly arylene sulfide excellent in mechanical strength, melting stability, a moldability, etc., in more detail about the manufacture approach of the poly arylene sulfide.
[0002]
[Description of the Prior Art] The poly arylene sulfides (the following, PAS, and brief sketch) represented by the polyphenylene sulfide (the following, PPS, and brief sketch) are engineering plastics excellent in thermal resistance, chemical resistance, fire retardancy, a mechanical strength, an electrical property, dimensional stability, etc. By the general melting processing methods, such as extrusion molding, injection molding, and compression molding, since it can fabricate for various mold goods, a film, a sheet, fiber, etc., PAS is used widely in extensive fields, such as electrical and electric equipment and Jidosha Kiki. Moreover, PAS is used also for the field of the powder coating to a metal or other ingredients.
[0003] Conventionally, the approach to which an alkali-metal sulfide and a dihalo aromatic compound are made to react is learned in organic amide solvents, such as a N-methyl-2-pyrrolidone, as the typical manufacture approach of PAS (JP,45-3368,B etc.). This reaction is a condensation-polymerization reaction which a polymer generates by the repeat of a dealkalization metal halide (for example, deNaCl) condensation reaction. In early stages of [development] PAS, since a high-polymer polymer was not able to be obtained, after carrying out the polymerization of the polymer of low polymerization degree, it heated under existence of air, partial bridge formation was performed, and macromolecule quantification was performed. Generally such PAS is called the bridge formation type. If oxidation bridge formation of the low polymerization degree PAS is heat-treated and carried out under existence of air, the reinforcement of the mold goods can be raised. However, from the first, since the bridge was considerably constructed over altitude in the polymer of low polymerization degree, mold goods with sufficient mechanical properties, such as toughness, were not able to be obtained. Moreover, the low polymerization degree PAS was difficult for melting stability to be bad and to control the melt viscosity by heat treatment or heating at the time of melting shaping in the range of desired, since melt viscosity goes up remarkably. Therefore, it was difficult to obtain the mold goods by which were inferior to fabricating-operation nature, and physical properties were stabilized.
[0004] Then, when making an alkali-metal sulfide and a dihalo aromatic compound react in an organic amide solvent, the method of obtaining the amount PAS of macromolecules at the time of a polymerization was developed by using alkali-metal carboxylate, such as an acetic-acid lithium, as a polymerization assistant (JP,52-12240,B). Generally such PAS is called the straight chain type.
[0005] On the other hand, generally the solvent flash method (solvent flashing process) was adopted in the past after polymerization reaction termination as an approach of collecting PAS from the reaction mixture containing an organic amide solvent, Generation PAS, byproduction alkali-metal halide (usually salt), an unreacted monomer, oligomer, etc. When this solvent flash method makes the interior of a room

of a pressure lower than that pressure spout the reaction mixture heated by the elevated temperature under application of pressure, it is an approach of collecting solvents using the phenomenon in which evaporation of a solvent takes place rapidly. However, adoption of a solvent flash method collects powder-like PAS from a reaction mixture. This powdered PAS had the problem that clearance of the intermingled oligomer, a low-molecular-weight impurity, etc. was difficult.
[0006] Then, the PAS slurry was made to form by adding a phase separation agent to the reaction mixture in an elevated-temperature condition, carrying out phase separation of the PAS dense phase from an organic amide solvent, and subsequently to the bottom of stirring cooling slowly after polymerization reaction termination, from the temperature to which PAS makes a melt phase, and the method of collecting granular PAS was proposed (JP,59-1536,A). As a phase separation agent, water, paraffin hydrocarbon, high-boiling point alcohol, the high-boiling point ether, etc. are illustrated. According to this approach, the slurry which contains the comparatively large and coarse granularity PAS from a reaction mixture can be made to generate. Therefore, by carrying out this slurry a ** exception, oligomer, a low-molecular-weight impurity, etc. can be removed with filtrate, and Granularity PAS can be collected. Moreover, this granularity PAS can remove an impurity easily further also by washing.
[0007] Moreover, the coexistence moisture content of ** system of reaction is adjusted low, a preceding paragraph polymerization reaction is performed, and in the approach of making an alkali-metal sulfide and a dihalo aromatic compound reacting in an organic amide solvent, and manufacturing PAS, reaction temperature is raised, and subsequently to ** system of reaction, while adding water and raising a coexistence moisture content, the approach of continuing a reaction is proposed until melt viscosity fully goes up (JP,63-33775,B). According to this two-step polymerization method, at a preceding paragraph polymerization process, since the coexistence moisture content is adjusted low, the side reaction and the decomposition reaction resulting from existence of moisture which are not desirable can be controlled. At a latter-part polymerization process, the generation polymer which is in a melting condition in an organic amide solvent carries out liquid-liquid phase separation by sufficient existence of a moisture content at a polymer dense phase and a polymer lean phase. At a latter-part polymerization process, under stirring of the system of reaction, since the pyrogenetic reaction in this phase separation condition is performed, the polymerization reaction in a polymer dense phase advances, and PAS of the amount of macromolecules can be obtained according to the shape of a straight chain. According to this approach, the amount PAS of macromolecules can be obtained, without using expensive polymerization assistants, such as an acetic-acid lithium. And after polymerization reaction termination, if a reaction mixture is cooled, the granularity PAS with a particle size large enough is recoverable. Filtration and washing can collect and refine this granularity PAS.
[0008] As mentioned above, the approach compound the amount PAS of macromolecules, and solid liquid separation collects granularity easy PAS by filtration, washes it, and refines it from a reaction mixture after polymerization reaction termination recently by using organic carboxylate, water, etc. as a polymerization assistant or a phase separation agent at the time of a polymerization is in use. However, such a recovery approach of Granularity PAS of the amount of macromolecules had the problem that cost started recovery of a solvent too much so that it might explain in full detail below.
[0009] That is, if it filters after making the slurry which cools a reaction mixture and contains Granularity PAS form, the organic amide solvent of a large quantity remains in the granularity PAS carried out the ** exception of what currently can collect many organic amide solvents. It is difficult to fully remove an organic amide solvent in rinsing, and it difficult after washing to carry out separation / purification processing of the mixed liquor containing alkali-metal halide (salt) etc. to the wash water of a large quantity, an organic amide solvent, and the organic amide solvent. Therefore, generally, the granularity PAS obtained after filtration and the wet cake containing an organic amide solvent etc. were washed using solvents for recovery, such as an acetone, and have removed the organic amide solvent. Rinsing is performed after this organic solvent washing, and water-soluble materials, such as salt, are removed. A low molecular weight constituent and a volatile component are also removed with an organic amide solvent by organic solvent washing. The solvent mixture containing the solvent for

recovery, an organic amide solvent, a low molecular weight constituent, etc. needs to process separation of an organic amide solvent, separation of the solvent for purification and recovery, purification, etc. after washing. However, the facility for it and energy are needed for such separation / purification processing of each solvent. Moreover, in order to refine the organic amide solvent collected from the slurry containing the above-mentioned granularity PAS by filtration, it is necessary to perform purification processing of reheating and distilling. These processings are the big factor which bars low-pricing of PAS.

[0010]

[Problem(s) to be Solved by the Invention] The object of this invention is among an organic amide solvent in the approach of making an alkali-metal sulfide and a dihalo aromatic compound reacting, and manufacturing the poly arylene sulfide under existence of phase separation agents, such as water, to offer the approach of manufacturing the poly arylene sulfide which aimed at sharp reduction of the cost accompanying recovery / purification processing of the organic amide solvent after polymerization reaction termination, and was excellent in mechanical strength, melting stability, a moldability, etc. this invention persons found out that said object could be attained by making an organic amide solvent evaporate or distill, and collecting them, after performing the phase separation polymerization by water addition, as a result of inquiring wholeheartedly, in order to conquer the trouble of said conventional technique.

[0011] The slurry containing the polymer which lowered the temperature of a reaction mixture to the bottom of stirring after reaction termination, granulated the generation polymer of a melting condition by the approach of carrying out the polymerization of the amount PAS of macromolecules conventionally using a phase separation agent or a polymerization assistant, and was granulated in the organic amide solvent was made to form, subsequently, this slurry was filtered and Granularity PAS was collected. The filtration from an organic amide solvent is easy for Granularity PAS, and it is also easy to remove impurities, such as a by-product, unreacted object, and low-molecular-weight object, by filtration and washing. However, as for this approach, cost increases to separation, purification, etc. of an organic amide solvent.

[0012] After performing the phase separation polymerization by water addition, this invention persons by collecting organic amide solvents with the application of evaporation or the distillation means of a flash plate etc. to a reaction mixture (1) Since evaporation or distillation of an organic amide solvent can be performed while a reaction mixture is in an elevated-temperature condition after polymerization reaction termination, that energy cost can be reduced and (2) -- by performing the evaporation or distillation of water which could collect organic amide solvents with comparatively high purity, and was used as a phase separation agent in advance of recovery of an organic amide solvent PAS obtained by carrying out a polymerization under existence of the purity of the organic amide solvent to collect being raised and (3) phase-separation agent Even if heat-treated unlike the conventional low polymerization degree PAS, there is no rapid lifting of melt viscosity, control of the melt viscosity by heat treatment is easy, and it found out that it could moreover obtain as a polymer which was excellent in mechanical strength, melting stability, a moldability, etc. after heat treatment.

[0013] In this invention, the water used as a phase separation agent after polymerization reaction termination and before organic amide solvent recovery is removable first by approaches, such as evaporation or distillation. In that case, when the water in a reaction mixture decreases in number, the rate which a part of alkali-metal halide [at least], such as salt which carried out the byproduction, deposits, and melts into a solvent decreases. Then, when an organic amide solvent is removed, the content of the alkali-metal halide in a polymer decreases, and, moreover, washing becomes possible easily by rinsing. If it heat-treats under the condition on which the melt viscosity of a polymer increases after drying the rinsed polymer, the low-molecular-weight object and volatile component which remain are removable.

[0014] Thus, according to the manufacture approach of this invention, in the middle of a polymerization reaction, water is added in the system of reaction, by combining the polymerization method (two step polymerization method of water addition) of PAS which carries out a phase separation polymerization,

and the method of dissociating / collecting the organic amide solvents by evaporation or distillation of a flash plate etc., PAS can be made to be able to generate by comparatively short polymerization time amount, and PAS excellent in a mechanical strength, melting stability, a moldability, etc. can be offered. Especially, in a two-step polymerization method, if a temperature-up polymerization method is adopted, compaction of polymerization time amount will become easy. Simultaneously, the cost concerning recovery of an organic amide solvent is substantially reducible. This invention comes to be completed based on these knowledge.

[0015]

[Means for Solving the Problem] In the approach of according to this invention making an alkali-metal sulfide and a dihalo aromatic compound reacting, and manufacturing the poly arylene sulfide in an organic amide solvent (A) While heating an organic amide solvent, an alkali-metal sulfide, and the mixture containing a dihalo aromatic compound and making them react Add water in the system of reaction and the water of the amount which is sufficient for making the liquid-liquid phase separation condition which consists of the dense phase and lean phase of a generation polymer by it form is made to exist at the event of the request during [from after reaction initiation] before reaction termination. Subsequently A pyrogenetic reaction is made to continue till reaction termination. And after (B) reaction termination, an organic amide solvent, The manufacture approach of the poly arylene sulfide characterized by including each process which is made to evaporate or distill an organic amide solvent, and collects them from a generation polymer, water, and the reaction mixture containing byproduction alkali-metal halide is offered.

[0016] The manufacture approach of this invention rinses the mixture containing the generation polymer which remains after the solvent recovery from the (C) reaction mixture, and byproduction alkali-metal halide after a solvent recovery process (B), and removes alkali-metal halide, and it is desirable to include further each process which dries the humid polymer after (D) rinsing. Moreover, as for the manufacture approach of this invention, it is desirable to heat-treat (E) desiccation polymer after a desiccation process (D), and to include further the process which increases the melt viscosity of a polymer.

[0017] In a reaction process (A), after reaction initiation, when the invert ratio of a dihalo aromatic compound becomes 50 - 98-mol the range which is %, while adding water and making a liquid-liquid phase separation condition form by it in the system of reaction, it is desirable to continue a pyrogenetic reaction till reaction termination in the state of this liquid-liquid phase separation. In a solvent recovery process (B), it is desirable to precede recovery of an organic amide solvent and to arrange the process which is made to evaporate or distill some [at least] water, and removes it from a reaction mixture.

[0018]

[Embodiment of the Invention] Hereafter, this invention is explained in full detail.

(Alkali-metal sulfide) As an alkali-metal sulfide used by this invention, a sulfuration lithium, a sodium sulfide, a potassium sulfide, a sulfuration rubidium, sulfuration caesium, two or more sorts of such mixture, etc. can be mentioned. These alkali-metal sulfides are usually marketed as a hydrate, and are used. As a hydrate, sodium-sulfide 9 monohydrate ($Na_2S.9H_2O$), sodium-sulfide 5 monohydrate ($Na_2S.5H_2O$), etc. are mentioned, for example. An alkali-metal sulfide may be used as aquosity mixture. Moreover, an alkali-metal sulfide is in in [a hydrogen sulfide or alkali-metal sulfhydrate, and an alkali-metal hydroxide to] an organic amide solvent. It can prepare by situ. An alkali-metal sulfide can also use what was prepared with other reaction cans. In order to make it react with the alkali-metal sulfhydrate and the alkali-metal thiosulfate which may recognize minute amount existence into an alkali-metal sulfide, an alkali-metal hydroxide can be used together and clearance or conversion to an alkali-metal sulfide can be performed for these minor constituents. Also in an alkali-metal sulfide, a sodium sulfide and a specific hydrosulfide are desirable especially from a cheap thing. In the manufacture approach of this invention, the moisture which should be dehydrated at a dehydration process is the above-mentioned water of hydration, the water medium of aquosity mixture, water that carries out a byproduction by the reaction of alkali-metal sulfhydrate and an alkali-metal hydroxide.

[0019] (Dihalo aromatic compound) The dihalo aromatic compound used by this invention is a dihalogen-ized aromatic compound which has two halogen atoms coupled directly with the ring. As an

example of a dihalo aromatic compound, o-dihalo benzene, m-dihalo benzene, p-dihalo benzene, dihalo toluene, dihalo naphthalene, methoxy-dihalo benzene, a dihalo biphenyl, a dihalo benzoic acid, dihalo diphenyl ether, dihalo diphenylsulfone, a dihalo diphenyl sulfoxide, dihalo diphenyl ketone, etc. are mentioned, for example. here, a halogen atom points out each atom of a fluorine, chlorine, a bromine, and iodine, and in the same dihalo aromatic compound, two halogen atoms may be the same, or may differ. in these dihalo aromatic compounds, two halogen atoms may be the same, or may differ. The dihalo aromatic compound may have one or more substituents, such as a cull BOSHIKIRU radical, a hydroxyl group, a nitro group, an amino group, and a sulfonic group. When a dihalo aromatic compound carries out two or more propers of the substituent, even when it is independent, even if the class of substituent is the combination of a different class, it is not cared about. These dihalo aromatic compound is independent, respectively, or can be used combining two or more sorts. The amount of the dihalo aromatic compound used in this invention is usually 0.9-1.2 mols to one mol of preparation alkali-metal sulfides.

[0020] (A regulator, branching and a cross linking agent) The end of Generation PAS can be denatured or a mono-halo compound (you may not necessarily be an aromatic compound) can be used together for adjusting a polymerization reaction and molecular weight etc. In order to make branching or the cross linked polymer generate, it is also possible to use together the poly halo compound (for you not to be necessarily an aromatic compound) which three or more halogen atoms combined, an active hydrogen content halogenated-aromatics compound, a halogenated-aromatics nitro compound, etc. As a poly halo compound as branching and a cross linking agent, TORIHARO benzene is mentioned preferably.

[0021] (Organic amide solvent) In this invention, an organic amide solvent (namely, aprotic polarity organic solvent) is used as a solvent of a polymerization reaction. As an example of an organic amide solvent, N.N-dimethylformamide, Amide compounds, such as N,N-dimethylacetamide; N-methyl-epsilon caprolactam, A N-methyl-2-pyrrolidone (hereafter referred to as NMP), N-alkyl pyrrolidone compound or N-cycloalkyl pyrrolidone compounds, such as an N-cyclohexyl-2-pyrrolidone; Tetra-alkylurea compound [, such as N, such as 1 and 3-dialkyl-2-imidazolidinone, and N-dialkyl imidazolidinone compound; tetramethylurea,]; Hexa alkyl phosphoric triamide compounds, such as hexamethylphosphoric triamide, etc. are mentioned. These organic amide solvents may be used independently, respectively, and may be used combining two or more kinds. Also in these organic amide solvents, N-alkyl pyrrolidone compound, N-cycloalkyl pyrrolidone compound and N, and N-dialkyl imidazolidinone compound is desirable, and NMP, N-methyl-epsilon caprolactam and 1, and 3-dialkyl-2-imidazolidinone is used especially preferably. The range of the 0.1-10kg of the amount of the organic amide solvent used used for the polymerization reaction of this invention is usually 0.15-1kg preferably per one mol of alkali-metal sulfides.

[0022] (Phase separation agent) In this invention, in order to promote a polymerization reaction and to obtain the amount PAS of macromolecules for a short time, water is used as a phase separation agent. Although phase separation agents other than water and water may be used together if needed, it is desirable to use a water independent or water as a principal component. If a phase separation agent is made to exist in the system of reaction, the generation polymer (a prepolymer is included) which is in a melting condition in an organic amide solvent will carry out liquid-liquid phase separation at a polymer dense phase and a polymer lean phase. If a pyrogenetic reaction is continued in the state of such phase separation, polymerization degree increases and the amount PAS of macromolecules can be obtained. A phase separation agent is made to exist in the system of reaction in sufficient amount for such phase separation to arise.

[0023] This invention is available for adding an organic carboxylic-acid metal salt, an organic sulfonic-acid metal salt, lithium halide, a phosphoric-acid alkali-metal salt, etc. auxiliary, although water is used as a phase separation agent. However, if these metal salts are used, the viscosity of the slurry generated by the polymerization reaction will become high, or impurities, such as a metal, will remain into the dry polymer, and the mechanical property and electrical characteristics of a polymer will fall. On the other hand, the element which is independent about water, or can make comparatively low viscosity of the polymerization reaction mixture obtained after a polymerization reaction by using water as a principal

component, and worsens the mechanical property and electrical characteristics of a polymer as a phase separation agent can be removed or controlled.

[0024] The amount of the phase separation agent used is range which usually becomes an excess of 2.0 mol, and ten mols or less preferably 0.01-10 mols to one mol of preparation alkali-metal sulfides. Although a part of phase separation agent may live together from the time of the preparation of a polymerization, it is desirable to adjust to sufficient amount to add a phase separation agent in the middle of a polymerization reaction, and form phase separation. In the approach of making an alkali-metal sulfide and a dihalo aromatic compound reacting, and manufacturing PAS in an organic amide solvent, in the preparation phase, a coexistence moisture content is adjusted in many cases, and some water of a phase separation agent usually lives together from a preparation phase in that case. However, if a lot of water exists from the early stages of a polymerization, since it will be easy to produce the side reaction and the decomposition reaction which are not desirable, it is desirable to control to within the limits which had the coexistence moisture content limited, to add water to the system of reaction in the middle of a polymerization reaction, and to adjust at the time of preparation, so that the whole coexistence moisture content may turn into a complement at phase separation.

[0025] (Polymerization reaction) In this invention, PAS is manufactured by making an alkali-metal sulfide and a dihalo aromatic compound react in an organic amide solvent. In this polymerization reaction, generally in advance of a polymerization process, heating dehydration of the mixture containing an organic amide solvent, an alkali-metal sulfide, and moisture is carried out, and the moisture content of a polymerization reaction system is adjusted (dehydration process). The constituent and dihalo aromatic compound which were obtained at the dehydration process concerned are mixed after a dehydration process, and the polymerization reaction of an alkali-metal sulfide and the dihalo aromatic compound is heated and carried out in an organic amide solvent (polymerization process).

[0026] (Dehydration process) A dehydration process heats an alkali-metal sulfide in an organic amide solvent under an inert gas ambient atmosphere desirably, and carries it out by separating water out of the system of reaction by distillation. In order to use an alkali-metal sulfide as a hydrate or aquosity mixture, it usually contains the moisture more than an initial complement. Moreover, when using alkali-metal sulfhydrate as a source of sulfur, the alkali-metal hydroxide of equimolar extent is added, and it is in about both in an organic amide solvent. It is made to react by situ and changes into an alkali-metal sulfide. At this conversion reaction, water carries out a byproduction. At a dehydration process, the moisture which consists of these water of hydration (water of crystallization), a water medium, byproduction water, etc. is dehydrated until it becomes within the limits of an initial complement. At a dehydration process, to one mol of alkali-metal sulfhydrates, the coexistence moisture content of a polymerization reaction system usually dehydrates until it becomes about 0.3-5 mols. In adopting a two-step polymerization method, 0.5-2.4 mols dehydrate preferably until it becomes about 0.5-2.0 mols more preferably. Since it is easy to produce the side reaction which is not desirable as for decomposition of a generation polymer etc. when a moisture content decreases too much at a dehydration process, it is desirable to add water before a polymerization process and to adjust to a desired moisture content.

[0027] Generally 300 degrees C of preparations of these raw materials are preferably performed in an ordinary temperature to 200 degrees C temperature requirement from ordinary temperature. The preparation sequence of a raw material is in random order, is good, and may add each raw material in the middle of dehydration actuation further. Said organic amide solvent is used as a solvent used for a dehydration process. As for this organic amide solvent, it is desirable that it is the same as that of the organic amide solvent used for a polymerization process, and it is desirable that both are especially NMP(s). The amount of the organic amide solvent used is usually 0.1-10kg per one mol of preparation alkali-metal sulfides.

[0028] Dehydration actuation is a 60 to 280 degrees C temperature requirement, and is performed by usually heating preferably 300 degrees C or less of constituents after teaching from for 15 minutes for for 30 minutes to 10 hours for 24 hours. The heating approach has the combination of the approach and the gradual or continuous warm up procedure holding constant temperature, or both approaches. A dehydration process is performed by the combination method of a batch type, continuous system, or

both methods etc. The equipment which performs a dehydration process may be the same as the reaction can or reaction vessel used for a polymerization process, or may differ. At a dehydration process, with water, some organic amide solvents carry out azeotropy, and it is usually discharged. Water separates an organic amide solvent and water by distillation as azeotropic mixture with an organic amide solvent, and is discharged only as water. In many cases, at a dehydration process, a hydrogen sulfide is discharged with the azeotropic mixture of water or water, and an organic amide solvent. It is possible to collect these hydrogen sulfides discharged by suitable approaches, such as absorption by the alkali water solution or the organic amide solvent, and to reuse them as sources of sulfur, such as an alkali-metal sulfide.

[0029] (Polymerization process) A polymerization process mixes the constituent and dihalo aromatic compound after dehydration process termination, and is performed by heating the mixture. In case this mixture is prepared, the amount of organic amide solvents, a coexistence moisture content, etc. are usually adjusted. Moreover, the additive of a polymerization assistant and others may be mixed in this case. 100-350 degrees C of mixing with the constituent and dihalo aromatic compound which were obtained after dehydration process termination are usually preferably performed in a 120-350-degree C temperature requirement. Especially a mixed sequence foreword does not have a limit and both components are selectively performed every [small quantity] or by adding at a stretch.

[0030] Generally 100-350 degrees C of polymerization reactions are preferably performed in 150-330 degrees C. The approach the heating approach holds constant temperature, a gradual or continuous warm up procedure, or the approach by the combination of law is both used. Generally, the range of polymerization reaction time amount is for [10 minutes] - 72 hours, and it is for [30 minutes] - 48 hours desirably. If the approach of this invention is adopted, in many cases, PAS of desirable physical properties is recoverable by the reaction time of 1 - 10 hours. Although the amount of the organic amide solvent used at a polymerization process is about 0.1-10kg, as long as it is this within the limits, it may usually change that amount per one mol of alkali-metal sulfides in the middle of a polymerization reaction, as described above.

[0031] the coexistence moisture content at the time of polymerization reaction initiation -- one mol of alkali-metal sulfhydrates -- receiving -- usually -- 0.5-2.4-mol 0.3-5 mols are about 0.5-2.0 mols more preferably. however -- the case where a special polymerization method is adopted to obtain a low-molecular-weight polymer and oligomer or -- a coexistence moisture content -- this -- it is good also as out of range. For example, 0.1-15 mols of coexistence moisture contents per one mol of alkali-metal sulfides can be preferably adjusted within the limits of 0.5-10 mols. However, in order to obtain the amount PAS of macromolecules with the application of the approach of this invention, it is usually desirable to adjust the coexistence moisture content in early stages of a polymerization reaction to said within the limits, and especially the thing for which a coexistence moisture content is adjusted within the limits of 0.5-2.0 mols to one mol of alkali-metal sulfides is desirable.

[0032] adding water in the system of reaction, making the liquid-liquid phase separation condition which consists of the dense phase and lean phase of a generation polymer by it form by the manufacture approach of this invention at the event of the request during [from after reaction initiation] before reaction termination, and continuing a pyrogenetic reaction in the condition -- the amount of macromolecules -- or PAS of the amount of macromolecules is made to generate comparatively As a phase separation agent, the reasons of clearance from cost and a polymer etc. to water is desirable. When making a coexistence moisture content increase and making a phase separation condition form, if the stage of water addition is from polymerization initiation before termination, it can be carried out to the time amount of arbitration. However, in order to control decomposition of a generation polymer, and occurrence of the side reaction which is not desirable, in many cases, the approach of lessening a coexistence moisture content, and the invert ratios of a monomer (for example, dihalo aromatic compound) being more than 50 mol % and the phase which became 50-98-mol % preferably, adding water in early stages of a polymerization reaction, and raising a coexistence moisture content to phase separation even at a complement is desirable. While making the water of a complement exist in phase separation and making a liquid-liquid phase separation condition form before the time of reaction

termination at least generally, it is desirable to continue a pyrogenetic reaction further in the state of this liquid-liquid phase separation, and to terminate a polymerization reaction.

[0033] As an approach to which a coexistence moisture content is made to increase in the middle of a polymerization reaction For example, (1) preceding paragraph process : in the condition that 0.5-2.0 mols [per one mol of preparation alkali-metal sulfides] water exists React in a 180-235-degree C temperature requirement, and a prepolymer is made to generate at invert ratio % of 50-98 mols of a dihalo aromatic compound. Subsequently (2) -- latter-part process:, while adding water so that it may be in the condition that an excess of 2.0 mol per one mol of preparation alkali-metal sulfides and water 10.0 mols or less exist in the system of reaction Temperature up is carried out into a 245-290-degree C temperature requirement, and there is the approach (JP,63-33775,B) of continuing a pyrogenetic reaction.

[0034] According to this two-step polymerization method, water can be used as a phase separation agent and PAS of the amount of macromolecules can be obtained. Especially at the latter-part polymerization process which a moisture content is increased and carries out pyrogenetic reaction continuation, since the water of a phase separation agent exists in sufficient amount, the generation polymer which is in a melting condition in an organic amide solvent carries out liquid-liquid phase separation at a polymer dense phase and a polymer lean phase. If a pyrogenetic reaction is continued in the state of this phase separation, the polymerization reaction in a polymer dense phase advances efficiently, and PAS of the amount of macromolecules can be obtained by the shape of a straight chain. If this two-step polymerization method is built into the approach of this invention, PAS which has physical properties also with the good polymerization reaction of the short time of less than 10 hours can be obtained.

[0035] Moreover, in such a two-step polymerization reaction, it can change to a latter-part polymerization process in a short time by carrying out carrying out temperature up of the preceding paragraph polymerization process. As desirable temperature-up polymerization conditions in this case, in the organic amide solvent containing 0.5-2.0 mols [per one mol of (1) process 1:preparation alkali-metal sulfides] water An alkali-metal sulfide and a dihalo aromatic compound are made to react in a 170-270-degree C temperature requirement. Make it react in that case, carrying out temperature up of the between from at least 220 degrees C to 240 degrees C of this temperature requirement with an average of 0.1-1-degree-C programming rate for /, and a prepolymer is made to generate at invert ratio % of 50-98 mols of a dihalo aromatic compound. Subsequently (2) While adding water at the temperature of 235 degrees C or more in the system of reaction so that it may be in the condition that an excess of process 2:2.0 mol per one mol of preparation alkali-metal sulfides and water ten mols or less exist There is the approach (JP,8-183858,A) of continuing a reaction in a 245-290-degree C temperature requirement.

[0036] In this invention, in addition to this, various well-known polymerization methods or the deformation approach of those can be applied, and it is not especially limited to a specific polymerization method. The combination of a batch type, continuous system, or both methods is sufficient as a polymerization reaction method. In a batch type polymerization, the method which uses two or more reaction cans for the object which shortens the polymerization cycle time may be used.

[0037] (Dehydration process after a polymerization reaction) In the manufacture approach of this invention, although organic amide solvents are collected from a reaction mixture after polymerization reaction termination, it is desirable to dehydrate a reaction mixture before this solvent recovery process. Holding the temperature at the time of polymerization reaction termination, to the temperature to which a polymer does not deposit, dehydration is lowered continuously or gradually and is performed. 180-290 degrees C of dehydration are usually preferably performed at the dehydration temperature of the range of 200-280 degrees C. If dehydration temperature exceeds 290 degrees C, the reaction which disassembly of a solvent etc. does not have will occur and it will become difficult to obtain predetermined melt viscosity and the polymer of molecular weight. Since much heat energy is needed in order for the recovery effectiveness of an organic amide solvent to fall or to gather recovery effectiveness in case evaporation or distillation recovers an organic amide solvent at degree process if dehydration temperature becomes lower than 180 degrees C, it is economically disadvantageous.

Dehydration time amount is usually for [5 minutes] - 10 hours preferably for for 1 minute to 12 hours.
[0038] Preferably, dehydration performs 1.8 mols or less of 2.0 mols or less of moisture contents in polymerization reaction mixture per one mol of preparation alkali-metal sulfides until it becomes 1.5 mols or less. A polymerization reaction tends [further] to advance also in the solvent recovery process concerned until it will result in the recovery process of the following organic amide solvent, if there are too many moisture contents in a reaction mixture, consequently the molecular weight of a generation polymer may change notably. Therefore, in order to obtain stably the homogeneous high polymer which has desired molecular weight, it is desirable to reduce the moisture content in a reaction mixture as much as possible at this dehydration process.
[0039] Dehydration is performed by separating the water in a reaction mixture by evaporation. The approach evaporation fractional distillation separates only water, and the approach of evaporating together with water and some organic amide solvents in a reaction mixture, and separating can be used in that case. Moreover, the sulfur compound generated by an unreacted dihalo aromatic compound, the regulator, branching and a cross linking agent, the unreacted alkali-metal sulfide, or its decomposition when it was dehydration evaporates or vaporizes. Although dissociating as it is is desirable, even if it collects together with a generation polymer, when washing or heat treatment can dissociate and remove easily, even if these compounds that evaporated or vaporized return these compounds into a reaction mixture during dehydration or after dehydration termination, they are not cared about. Although dehydration is usually performed in the state of application of pressure and the pressure in a system decreases with progress of dehydration, you may carry out by application of pressure or reduced pressure actuation, maintaining a constant pressure. Dehydration can also be performed by ordinary pressure. Application of pressure or reduced pressure can be performed, and the pressure in a system can be adjusted so that it may become a pressure suitable for degree process after dehydration termination if needed.
[0040] (Recovery of a polymerization solvent) In the manufacture approach of this invention, an organic amide solvent is made to evaporate or distill, and are collected from the reaction mixture which contains an organic amide solvent, a generation polymer, a phase separation agent, and byproduction alkali-metal halide after polymerization reaction termination. In a reaction mixture, low-molecular-weight objects, such as an unreacted monomer and oligomer, various additives, etc. are usually contained in addition to each above-mentioned component (when it adds). Alkali-metal halide is usually salt.
[0041] In order to collect organic amide solvents from a reaction mixture by evaporation (volatilization is included) or distillation, the reaction mixture in an elevated-temperature condition is made to usually evaporate or distill. Under the present circumstances, if there is need, a reaction mixture is heated or reheated and can be adjusted to temperature required for evaporation or distillation. Since recovery of an organic amide solvent and a generation polymer being easy and operability are good, the method of evaporating an organic amide solvent and collecting them with a solvent flash method, is desirable. In advance of recovery of an organic amide solvent, the homogeneous high polymer of melt viscosity or molecular weight can be obtained by distilling off the water in a reaction mixture. Moreover, by dehydration, in next washing, it becomes easy to separate byproduction alkali-metal halide from a generation polymer, and the content of the metal component in the last polymer decreases. Furthermore, the recovery and purity of an organic amide solvent are improvable with dehydration.
[0042] Generally a solvent flash method can be widely performed by the known approach. Specifically, the method of making the tank for flash plates introduce and evaporate the reaction mixture in an elevated-temperature condition through a nozzle is mentioned after polymerization reaction termination. Under the present circumstances, in order to raise the recovery effectiveness of an organic amide solvent, it is desirable to make the inside of the tank for flash plates a vacuum or reduced pressure. Moreover, a gas can also be circulated, in order to discharge efficiently the organic amide solvent which evaporated within the flash tank and to collect them out of the tank for flash plates. As this gas, inert gas is desirable. As this inert gas, nitrogen gas, carbon dioxide gas, a steam, etc. can be mentioned. Also in these, nitrogen gas is desirable in respect of cost.
[0043] polymerization reaction mixture -- a batch -- it introduces into the tank for flash plates, letting

pass and carrying out the solvent flash plate of the nozzle combining these-like (a batch ---like) or continuously. When recovery of an organic amide solvent is inadequate, it is also possible to supply heat and to raise recovery separately, in a flash plate system. As a method of supplying heat, the approach of warming the tank for flash plates with a band heater etc. can be mentioned, for example. In order to promote blowdown out of the tank for flash plates of the organic amide solvent which evaporated, when circulating a gas, the approach of supplying heat can also be adopted by warming this gas and circulating it. Moreover, after discharging, discharging the mixture which carried out the flash plate from the tank for flash plates, heat can be supplied, it can be made a vacuum and reduced pressure, or the recovery of an organic amide solvent can also be further raised combining these.
[0044] In case a flash plate is carried out, the temperature of the reaction mixture supplied to the tank for flash plates takes into consideration the boiling point, the pressure in the tank for flash plates, etc., and adjusts them to the temperature to which the rate of solvent recovery becomes high. For example, when NMP is used as an organic amide solvent, it is usually preferably desirable 220 degrees C or more to consider as 240 degrees C or more more preferably 200 degrees C or more. the mixture which carried out the flash plate -- a batch -- it takes out from the tank for flash plates combining these-like (a batch --- like) or continuously. Thus, evaporation or distillation actuation of a solvent flash method etc. separates an organic amide solvent and other components from a reaction mixture. This solvent recovery process recovers an organic amide solvent with 95% or more of recovery 90% or more 80% or more preferably. In many cases, an organic amide solvent is recoverable from a reaction mixture with 98% or more of recovery.
[0045] The component which remains after solvent recovery is the mixture containing a generation polymer and byproduction alkali-metal halide, and is usually a solid. As a phase separation agent, when an organic sulfonic-acid metal salt, lithium halide and an organic carboxylic-acid metal salt, a phosphoric-acid alkali-metal salt, etc. are used, these metal salts are also contained in solid mixture (solid content). Moreover, low molecular weight constituents and various additives, such as oligomer, are also contained in solid content (when it adds). As for the amount of the organic amide solvent which remains in such solid content, it is desirable to consider as 2 or less % of the weight more preferably 5 or less % of the weight to a generation polymer by seeing from the point of solvent recovery effectiveness. The generation polymer is contained in the solid content which remains after solvent recovery with the gestalt of the shape of powdered or a grain. When the temperature of the mixture at the time of solvent recovery is low to sufficient extent to form the slurry containing the granulated generation polymer, it is easy to granulate, and if it is an elevated temperature, it will be easy to become powder-like.
[0046] (Rinsing) In this invention, the mixture (solid content) containing the generation polymer which remains after solvent recovery, and byproduction alkali-metal halide is rinsed, and alkali-metal halide is removed. It is removed by this rinsing process when the metal salt (phase separation agent) of fusibility exists in water in solid content. Rinsing can be performed combining a batch type, continuous system, and these. In the case of a batch type, rinsing is desirable, stirring. the weight ratio of **** PAS at this time -- water / PAS=2-15 -- it is 5-10 preferably. It is for 5 - 30 minutes more preferably for 1 - 60 minutes that there should just be time amount sufficient as time amount per washing to fully dissolve the alkali-metal halide like salt and other water-soluble impurities.
[0047] If the so-called rinse actuation of permuting with water the wash water contained in solid content is performed after carrying out a ** exception [wash water] by making into solid content PAS which contains wash water after rinsing, the effectiveness of rinsing can improve and reduction of the count of rinsing can be aimed at. As a count of washing by water, it is 4 times or more more preferably once or more. If temperature of the water at the time of rinsing is made high, the clearance effectiveness of water-soluble impurities, such as salt, will become high. However, since it is disadvantageous in cost if the count of rinsing at an elevated temperature is made [many / not much], the count of rinsing in an elevated temperature is usually 2 or less times preferably 3 or less times. Of course, washing with high temperature hot water may be omitted. 120-270 degrees C of water temperature of elevated-temperature washing are usually 150-200 degrees C preferably.
[0048] Although washing of the solid content containing a generation polymer is fundamentally

performed only with water in this invention, as long as there is need, organic solvent washing of an acetone etc. may be performed. Moreover, in order to make the following desiccation process easy, washing with low-boiling point solvents, such as water and affinitive alcohol, may be performed. In these penetrant removers, recovery of the solvent with which it used only small quantity for washing since the organic amide solvent was not contained is easy. Moreover, there is also little amount of washing used and it ends. However, in order to avoid the cost high, it is desirable to control the amount of these solvents for washing used as much as possible, and to wash it only with water further. In addition, PAS can also be processed in the water solution containing salts, such as an acid and an ammonium chloride.

[0049] (Desiccation) It rinses by doing in this way, and from the solid content obtained at the solvent recovery process, the water-soluble materials which use alkali-metal halide, such as salt, as a principal component are fully removed, and it dries by the usual approach the appropriate back. Although especially drying temperature is not limited, it is desirable to carry out under a dry heat ambient atmosphere 100 degrees C or more from a viewpoint of drying efficiency. Although the upper limit of drying temperature is based also on the drying time, it is desirable that PAS considers as the conditions in which viscosity lifting by air oxidation does not occur substantially, and it is desirable from this viewpoint. [of less than 150 degrees C] However, it is employable, if the moisture of a polymer particle front face can be removed by short-time desiccation and it is not substantially accompanied by viscosity lifting, even if it is an elevated temperature to about 200 degrees C.

[0050] Both of the approaches, a batch type and continuous system, are possible for desiccation. Moreover, it can also be operated combining these approaches. In addition, when drying with continuous system, by adjusting temperature distribution and polymer distribution in an oven, it can include to heat treatment after desiccation, and can also carry out continuously. In many cases, adoption of the powdered or granular solvent flash method in an elevated temperature obtains PAS obtained according to a polymerization process, a solvent recovery process, an aforementioned rinsing process, and an aforementioned desiccation process as fine particles with a mean particle diameter of 10-200 micrometers. moreover, PAS obtained -- the amount of macromolecules -- or -- comparatively -- the polymer of the amount of macromolecules -- it is -- the melt viscosity (it measures in 310 degrees C and the 1200/second of shear rates) -- usually -- 5 or more Pa-s is 10 or more Pa-s more preferably more than 3Pa-s.

[0051] (Heat treatment) although the by-product of water solubility [polymer / which was obtained according to said desiccation process / desiccation], such as alkali-metal halide, the impurity, the additive, etc. are removed -- water -- an insoluble volatile component or an insoluble low molecular weight constituent are not removed. Since these components cause nonconformity at the time of the fabricating operation of PAS, it is desirable to remove or decrease by heat treatment in an elevated temperature. That is, in this invention, a desiccation polymer is heat-treated under the conditions on which the melt viscosity increases. The description of this desiccation polymer is in the R/C of melt viscosity being small, when it heat-treats under existence of oxygen (usually inside of air). Therefore, while a volatile component and a low-molecular-weight object are removable by heat-treating this desiccation polymer under the conditions on which that melt viscosity goes up, desired viscosity can be made to be able to thicken and it can consider as the polymer which was excellent in many physical properties, such as a mechanical strength, with it. On the other hand, if the polymer manufactured without using a phase separation agent is heat-treated, the R/C of melt viscosity will be high and, moreover, only the polymer inferior to a mechanical strength will be obtained.

[0052] Heat treatment in the approach of this invention is usually performed preferably 150 degrees C or more and below the melting point of a polymer in 200 degrees C or more and a temperature requirement with a melting point [of a polymer] of -10 degrees C. By this heat treatment, the melt viscosity (310 degrees C, 1200/second of shear rates) of a desiccation polymer is increased. Although especially the R/C of melt viscosity is not limited, it is usually preferably raised by the R/C of 1.5 times or more by 1.3 or more times. If the R/C of melt viscosity is too low, when the melt viscosity of a desiccation polymer is not sufficiently high, the improvement effect of a mechanical strength will become [the clearance

effectiveness of a volatile component or a low-molecular-weight object] low small. It is possible for there to be especially no upper limit of the R/C of the melt viscosity by heat treatment, and to also make it go up to 10 times or about 15 times if needed. As for the R/C of such melt viscosity, it is convenient to make into a criterion the case where a desiccation polymer is heat-treated on the heat treatment conditions of 260 degrees C / 2 hours in air, when the physical properties of a polymer are specified.
[0053] Both of the approaches, continuous system and a batch type, are possible for heat treatment. Heat treatment can be performed using a usual oven or a usual thermal treatment equipment. Although in a standing condition is sufficient as it, when heat-treating the polymer of a large quantity to homogeneity, as for a polymer, it is desirable to make a polymer particle flow by a certain approach. The approach of using an oven or a thermal treatment equipment equipped with stirring feather, the paddle, or the stirring screw as an approach of heat-treating, while making a polymer particle flow is mentioned.
[0054] Although heat treatment is usually performed in air, a request can also perform under reduced pressure under the ambient atmosphere of hypoxia concentration, or the ambient atmosphere where nitrogen gas, carbon dioxide gas, or a steam etc. is inactive. However, although the R/C of melt viscosity can be stopped low and there is a merit that extent of coloring is also small when it heat-treats under the ambient atmosphere in which oxygen does not exist, heat treatment cost becomes high. As for heat treatment, it is [among these] most desirable in cost to carry out in air. Although the R/C of the melt viscosity of PAS will become comparatively high if it heat-treats under the oxidizing atmosphere in air etc., on the other hand, the moldability of a polymer and the machine physical properties of a moldings are improved in many cases. That is, generally PAS obtained by carrying out a polymerization under existence of a phase separation agent is the straight chain-like amount polymer of macromolecules, and since melting stability is good, even if it raises melt viscosity, does not have lowering of mechanical physical properties and improves rather in many cases. Although the desiccation polymer in this invention has good melting stability, the polymer obtained after heat treatment also has good melting stability, and it is excellent in the moldability at the time of the usual melting fabricating operation.
[0055] (Generation polymer) In the manufacture approach of this invention, the melt viscosity of PAS which passed through the heat treatment process is arbitrary. This PAS is independent, or can blend various inorganic bulking agent, fibrous bulking agent, and various synthetic resin, an elastomer, a stabilizer, lubricant, a coloring agent, an antistatic agent, etc. by request, and can fabricate a sheet, a film, fiber, a pipe, various shaping components, etc. by the various fabricating methods, such as injection molding, extrusion molding, and compression molding. Moreover, PAS can be used also as powder coatings etc. with fine particles.
[0056]
[Example] Although an example and the example of a comparison are given and this invention is explained more concretely hereafter, this invention is not limited to these examples. In addition, the measuring method of physical properties is as follows.
(1) The melt viscosity of a melt viscosity polymer was measured in the temperature of 310 degrees C, and the 1200/second of shear rates.
(2) Machine physical properties (tensile strength, flexural strength) are ASTM about tensile strength. About D638 and flexural strength, it is ASTM. According to D790, it measured, respectively.
[0057] [Example 1]
(Polymerization) 3,800g of a sodium sulfide and 5 monohydrates containing NMP6,000g and 46.30% of the weight of a sodium sulfide (Na_2S) is taught, temperature up was gradually carried out to the 20l. autoclave (reaction can) to 200 degrees C at nitrogen gas, stirring over 3.5 hours after a permutation, and NMP1,100g was made to **** to it with 1,650g of water. Under the present circumstances, 0.50 mols H_2S vaporized. Therefore, effective Na_2S in the can after a dehydration process became 22.04 mols. Under [the amount of H_2S vaporization is equivalent to 2.22 mol% of preparation Na_2S]. The reaction can containing effective 22.04-mol Na_2S is cooled to 180 degrees C after the above-mentioned dehydration process. 3435g (pDCB) [pDCB/Na_2S=1.06 (mole ratio)] of p-dichlorobenzene, the sum total in NMP2815g and 183g [can of water -- amount of water -- NaOH13.3g of 97% of purity was

added so that /Na2 S=1.40(mole ratio)] and the amount of sum total NaOH(s) in a can might become 6.00-mol % to effective Na2 S. In addition, in the reaction can, NaOH (1.00 mols) generated when H2 S vaporized is contained. It was made to react at 220 degrees C for 4.5 hours, stirring an agitator by 250rpm (preceding-paragraph polymerization process: invert ratio [of a dihalo aromatic compound] = about 90-mol %). then -- while raising the number of stirring to 400rpm and continuing stirring -- 417g of water as a phase separation agent -- pressing fit -- the sum total in [can -- amount of water -- /Na2 S=2.45(mole ratio)] -- subsequently to 260 degrees C, temperature up was carried out and it was made to react for 1.0 hours (latter-part polymerization process: phase separation polymerization) In addition, the total polymerization time amount at this time was 5.5 hours.
[0058] (Dehydration after a polymerization reaction) The bulb attached in the reaction can upper part was released maintaining stirring maintaining the temperature after polymerization termination and in a can at 260 degrees C, and 655g water was distilled out through the distilling column. Little pDCB was also ****(ed) on that occasion. The amount of the distilled-out water is 1.65 mols per mol of brewing effective Na2 S, consequently the amount of water left behind in the can became 0.8 mols per mol of residual Nain can2 S.
(Flash plate actuation) The contents in a reaction can were transported for the bulb for distilling out to the tank for flash plates of capacity 80L through the nozzle after dehydration by the pressure of closing and nitrogen. At this time, nitrogen gas is circulated in the tank for flash plates, volatilizing NMP was discharged out of the tank for flash plates, and cooling uptake was carried out by the capacitor. NMP by which uptake was carried out was 7,632g (NMP recovery = 99%). 5,100g of solid content containing an PPS polymer and a sodium chloride was obtained.
(Rinsing and desiccation) To PPS contained in the solid content obtained by flash plate actuation, the water of an amount was added 10 times by weight, it washed for 15 minutes at a room temperature and 170 degrees C, and the wet polymer which repeated separation of the solid content by suction filtration a total of 4 times, and was obtained was dried at 105 degrees C for 8 hours. The yield of PPS after desiccation was 2,309g (yield = 97%). Moreover, the melt viscosity of PPS was 16 Pa-s. The sodium content in a polymer was 1,680 ppm.
(Heat treatment) In a part of this polymer, when heat treatment of 260 degrees C / 2 hours was performed in air circuit system oven, melt viscosity went up to 36Pa and s. It was 2.3 times the melt viscosity R/C at this time of this.
[0059] In the [example 1 of comparison] example 1, in the dehydration process after having not added water at a latter-part polymerization process, and a polymerization reaction, it carried out similarly and Desiccation PPS was obtained except having dehydrated 240g water (0.6 mols [per mol] water of brewing effective Na2 S). The total polymerization time amount at this time was 5.5 hours as well as the example 1. The melt viscosity of the obtained desiccation PPS was 8 Pa-s. In a part of this polymer, when air circuit system oven performed heat treatment of 260 degrees C / 2 hours, melt viscosity increased even to 53Pa and s, and it was 6.6 times the melt viscosity R/C at this time of this.
[0060] In the example 1 of the [example 2 of comparison] comparison, it carried out like the example 1 of a comparison except [all] performing preceding paragraph polymerization time amount in 10 hours. The total polymerization time amount at this time was 11 hours. The melt viscosity after desiccation of this PPS was 20 Pa-s. In a part of this polymer, when air circuit system oven performed heat treatment of 260 degrees C / 2 hours, melt viscosity increased even to 86Pa and s, and it was 4.3 times the melt viscosity R/C at this time of this.
[0061] Like the [example 2] example 1, the dehydration process was performed and brewing actuation was performed. Whenever [can internal temperature] fell to 140 degrees C. Stirring by 250rpm with an agitator, temperature up was carried out from 140 degrees C to 180 degrees C, having can internal temperature bet it for 30 minutes, and subsequently, from 180 degrees C to 220 degrees C, whenever [can internal temperature] was bet for 60 minutes, and carried out temperature up (the conversion of the halogen radical of the dihalo aromatic compound at this time was 29%). The event of amounting to 220 degrees C whenever [reaction can internal temperature] was made into the start time of a preceding paragraph polymerization process. Subsequently, the between from 220 degrees C to 240 degrees C was

applied for 60 minutes, and carried out continuation temperature up (average programming rate = a part for 0.33-degree-C/) (the conversion of the halogen of a dihalo aromatic compound became 78%). Furthermore, from 240 degrees C to 260 degrees C, it applied for 30 minutes, continuation temperature up was carried out (a part for average programming-rate/of 0.67 degrees C), and the preceding paragraph polymerization was ended. The time amount which the preceding paragraph polymerization took was a total of 90 minutes (1.5 hours) (the invert ratio of a dihalo aromatic compound = about 90-mol %). After preceding paragraph polymerization termination, promptly, the rotational frequency of an agitator was pressed fit by raising and 417g of water was pressed fit even in 400rpm at 260 degrees C (the sum total in a can amount of water being a mol ratio to brewing effective Na2 S 2.45 mol/mol). At this time, whenever [can internal temperature] fell a little. The event of returning to 260 degrees C again was made into the start time of a latter-part polymerization process. It held at 260 degrees C and was made to react for 1 hour. The time amount which the latter-part polymerization took was 60 minutes (1 hour). The sum total of the polymerization time amount of the preceding paragraph and the latter part was 2.5 hours. All actuation of dehydration after polymerization reaction termination, flash plate actuation, desiccation, heat treatment, etc. was performed like the example 1.

[0062] In the [example 3 of comparison] example 2, all adding-in latter-part polymerization-water ****** were carried out like the example 2. The above result is shown in a table 1.

[0063]

[A table 1]

	前段重合時間 (h)	後段重合時間 (h)	合計重合時間 (h)	後段重合時の水添加	乾燥後粘度 (Pa.s)	空気中260℃/2時間熱処理後粘度 (Pa.s)	粘度上昇率 (倍)
実施例1	4.5	1.0	5.5	有り	16	36	2.3
比較例1	4.5	1.0	5.5	無し	8	53	6.6
比較例2	10.0	1.0	11.0	無し	20	86	4.3
実施例2	1.5	1.0	2.5	有り	23	82	3.6
比較例3	1.5	1.0	2.5	無し	3	43	14.3

[0064] According to the manufacture approach of this invention, polymerization solvents can be collected with high recovery with a flash method, and PPS excellent in practicability can be obtained according to subsequent rinsing, desiccation, and a heat treatment process. According to the approach of this invention, melting stability can obtain good PPS and can thicken to desired melt viscosity by heat treatment so that clearly from the result of a table 1. Moreover, in the approach of this invention, in a latter-part polymerization, melt viscosity is high, and the viscosity R/C at the time of heat treatment is low, and by the short-time polymerization, by adding the water as a phase separation agent shows that a polymer with easy viscosity control is obtained, when raising viscosity by heat treatment. Moreover, it was shown clearly that the desiccation polymer obtained by being able to shorten preceding paragraph polymerization time amount substantially, adding water succeedingly, and performing a latter-part polymerization by adopting a temperature-up polymerization method as the preceding paragraph polymerization before water addition has high melt viscosity, and the melt viscosity R/C at the time of heat treatment is low. Therefore, in the approach of this invention, the advantage of combining with a specific two-step polymerization method is shown (examples 1 and 2). On the other hand, when it heat-treats on the conditions that it is the same when not adding water in a latter-part polymerization, the viscosity R/C at the time of heat treatment is large, and the polymerization time amount of long duration is required. In order melt viscosity is high and to prepare PPS with the low melt viscosity R/C at the time of heat treatment for a short time, it is effective to add the water as a phase separation agent in the latter part of a polymerization.

[0065] It carried out to the latter-part phase separation polymerization like the [example 4 of

comparison] example 1. Recovery of the polymerization solvent by the recovery solvent (acetone), rinsing, and desiccation were performed the ** exception of a polymer as shown below instead of collecting polymerization solvents (NMP) by flash plate actuation. After reaction termination, after cooling to near a room temperature, maintaining stirring, screen analysis of the granular polymer was carried out to the screen of 100 meshes through contents, and, specifically, it dissociated with the polymerization solvent. In order to collect NMP(s) which remain in a polymer, acetone ** was performed twice. Furthermore, it rinsed 4 times and the washing polymer was obtained. The obtained granular polymer was dried at 105 degrees C for 3 hours. Thus, the yield of the granular polymer of the shape of an acquired straight chain was 85%, and melt viscosity was 51Paands. By this approach, 85% and since [low and] pulverized coal etc. is removed, and there are few hypoviscosity objects, as for yield, melt viscosity is [although a granular polymer is obtained,] high.
[0066] The machine physical properties of the injection-molding object of each heat treatment polymer which heat-treated each polymer obtained in the <measurement of mechanical physical properties> example 1 and the example 1 of a comparison, and the polymer obtained in the example 4 of a comparison were investigated. In order to arrange the melt viscosity of these polymers, about the polymer after desiccation obtained in the example 1, it heat-treated at 260 degrees C in air circuit system oven for 5 hours, and melt viscosity obtained the polymer of 56Pa and s. About the polymer after desiccation obtained in the example 1 of a comparison, it heat-treated at 260 degrees C for 2 hours, and melt viscosity obtained the polymer of 53Pa and s. About the polymer (viscosity =51Paands) obtained in the example 4 of a comparison, it was used as it is. Each polymer 59.6 weight section, the glass fiber (diameter of 13 micrometers) 40 weight section, and the pentaerythritol tetra-stearate (PETS) 0.4 weight section were blended, melting kneading was carried out using the twin screw extruder, and the PPS resin constituent was produced. Thus, using the obtained class product, the test piece was fabricated by the injection-molding method, and tensile strength and flexural strength were measured. A result is shown in a table 2.
[0067]
[A table 2]

	重合溶剤回収方法	水添加	乾燥後粘度 (Pa.s)	熱処理後粘度 (Pa.s)	引張強度 (MPa)	曲げ強度 (MPa)
実施例1	フラッシュ	有り	16	56	168	194
比較例1	フラッシュ	無し	8	53	145	182
比較例4	濾過ー溶剤抽出	有り	51	–	176	201

[0068] An example 1, the example 1 of a comparison, and the comparison of a result show that the machine physical properties excellent in the direction where the melt viscosity before heat treatment used the large thing are shown, when heat treatment adjusts to comparable melt viscosity. Moreover, if the melt viscosity before heat treatment performs viscosity lifting by heat treatment from the comparison with an example 1 and the example 4 of a comparison using a large thing, equal machine physical properties can be acquired compared with the case where the shape of a straight chain PPS (example 4 of a comparison) which has comparable viscosity is used.
[0069] In the [example 3] example 1, after dehydrating after latter-part polymerization termination, it carried out like the example 1 except [all] having held for 12 hours, maintaining the temperature in a can at 260 degrees C. The yield of PPS after desiccation was 2,285g (yield = 96%), and melt viscosity was 15 Pa-s. Moreover, the sodium content in a polymer was 1,710 ppm. When this polymer was heat-treated like the example 1, melt viscosity went up to 37Pa and s, and it was 2.5 times the melt viscosity R/C at this time of this. Thus, when it dehydrates after polymerization reaction termination, there is little change of the melt viscosity of the polymer obtained even if it carries out long duration (12 hours) maintenance at an elevated temperature, and even if it heat-treats the obtained polymer, it turns out that the melt viscosity R/C also seldom changes. Moreover, the sodium content in a polymer is also known

by that it is few.
[0070] In the [example 4] example 1, it carried out like the example 1 except [all] having held for 12 hours, maintaining the temperature in a can at 260 degrees C, without dehydrating after latter-part polymerization termination. NMP by which uptake was carried out with the flash plate is 7,564g (NMP recovery = 98%), and obtained 5,150g of solid content containing an PPS polymer and a sodium chloride. The yield of PPS after performing washing and desiccation like an example 1 was 2,273g (yield = 96%), and melt viscosity was 45 Pa-s. Moreover, the sodium content in a polymer was 1,890 ppm. When this polymer was heat-treated like the example 1, melt viscosity went up to 89Pa and s, and it was 2.0 times the melt viscosity R/C at this time of this. Thus, when long duration (12 hours) maintenance of the elevated-temperature condition is carried out without dehydrating after polymerization reaction termination, it turns out that the melt viscosity of the polymer obtained increases greatly and a sodium content also increases. That is, the thing stably acquired for the polymer which has desired melt viscosity and molecular weight since a polymerization reaction will advance and melt viscosity and molecular weight will change remarkably, if the holding time in the elevated temperature of a reaction mixture becomes long, such as applying a flash method as it is, without dehydrating after polymerization reaction termination, becomes difficult. Moreover, if the sodium content in a polymer becomes large, electrical characteristics will fall. Therefore, it is desirable to arrange a dehydration process after polymerization reaction termination.
[0071]
[Effect of the Invention] According to the manufacture approach of this invention, since solvent recovery can be performed by low cost, PAS can be manufactured cheaply. Moreover, since the polymerization which uses water as a phase separation agent is performed, PAS of the amount of macromolecules is obtained comparatively for a short time. What is necessary is just to perform moderate heat treatment, although PAS of desired melt viscosity is obtained if it heat-treats after obtaining PAS with comparatively high melt viscosity at the process of a polymerization, solvent recovery, rinsing, and desiccation. Since the melt viscosity R/C at the time of heat treatment is low, control of melt viscosity is easy for PAS obtained by the approach of this invention, and it is easy to obtain PAS of desired melt viscosity. Therefore, few objects of the variation in many properties are obtained also for the mold goods which there is little lot-to-lot variation of melt viscosity, can process a polymer into stability, and are obtained. Moreover, after polymerization reaction termination, if solvent recovery is performed after dehydrating a reaction mixture, PAS which has desired melt viscosity and molecular weight can be obtained stably, and PAS with few contents of a metal component can be obtained.

[Translation done.]